

The Halochromism of Ketones

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The Halochromism of Ketones. II¹

BY LEIGH C. ANDERSON AND C. M. GOODING

Absorption spectra data which have been reported from this Laboratory² show that although benzophenone dissolves in ether to give colorless and in sulfuric acid to give colored solutions, the same absorption bands are obtained in each case. The band associated with the carbonyl group was found to be much more intense in the acid solution and the yellow color of the solution was caused by the widening of the base of this band until it extended into the visible region. Since the carbonyl band was intensified and no new bands appeared, we concluded that the colored solute had been produced through the reactivity of the carbonyl group. The fact that the same bands appear in both the colorless and colored solutions is evidence that this is a case of true halochromism as originally defined by Baeyer.³ This paper presents additional data which constitute conclusive evidence: first, that in the ketones we have studied the reactivity of the carbonyl group alone is responsible for the color in those cases where we find true halochromism; second, that the addition compounds produced with reagents like sulfuric acid and stannic chloride in the presence of hydrogen chloride do not involve the loss of the carbonyl group by addition to the carbonyl double bond; third, that some ketones give a colored solution in sulfuric acid and in addition to the enhancement of the carbonyl band, new bands are produced which we believe to be due to quinoidation, thereby showing two effects which can contribute to the formation of

color. In the case of the ketone chlorides, the absorption spectra of their colored solutions with stannic chloride or sulfuric acid are entirely different from those of the corresponding ethylene dichloride solutions. We believe that the color in these solutions is due to quinoidation and not to halochromism. These cases will be discussed later in the paper.

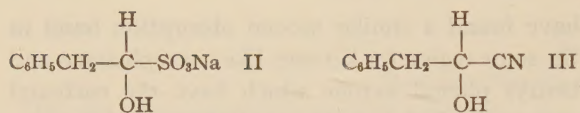
Comparisons of the absorption spectra of sulfuric acid solutions of 4-phenyl- and 4,4'-diphenylbenzophenone with corresponding ethylene dichloride solutions show that these are cases of true halochromism (Figs. 1 and 2). Solutions of these compounds, as well as benzophenone (Fig. 3), in mixtures of ethylene dichloride and stannic chloride give absorption curves which are very similar to those obtained for the corresponding ketone in sulfuric acid. The principal differences noted are that with stannic chloride the band having a maximum in the carbonyl region is displaced toward longer wave lengths (Table I) and is not quite as intense. In these cases, therefore, true halochromism is produced by either stannic chloride or sulfuric acid.

In all ketones that have been studied the absorption spectra of their colored solutions, whether the color is caused by sulfuric acid or stannic chloride, show marked enhancement of the absorption band which occurs in the carbonyl region of the spectrum and a shift of this band toward longer wave lengths. In order to see whether these changes were due to the rearrangement of an aromatic ring with formation of a new chromophore as, for example, the quinonoid nucleus, solutions of a number of aliphatic ketones were separately prepared in ethylene dichloride and sulfuric acid and the absorption spectra determined. The data show that the absorption

(1) The material in this paper comprises a portion of a thesis presented by C. M. Gooding to the Graduate School of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1934.

(2) Anderson, *THIS JOURNAL*, 55, 2094 (1933).

(3) In the discussion that follows we shall define as examples of true halochromism those solutions where the absorption spectra show that the color is produced through enhancement of the carbonyl absorption band without the production of new bands.



The fact, then, that the carbonyl band is not diminished and on the contrary is found to be very greatly enhanced on solution of our ketones in

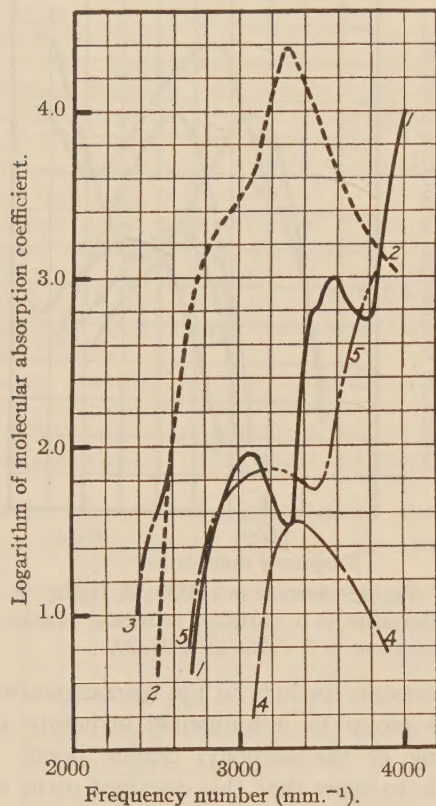
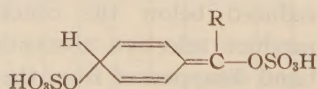
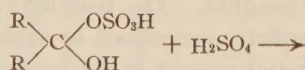
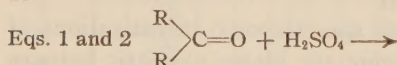


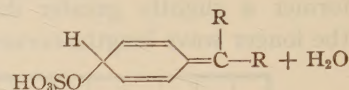
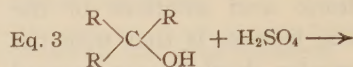
Fig. 5.—Cyclohexyl phenyl ketone: 1, in $\text{C}_2\text{H}_4\text{Cl}_2$; 2, H_2SO_4 ; 3, H_2SO_4 (after standing). Dicyclohexyl ketone: 4, $\text{C}_2\text{H}_4\text{Cl}_2$; 5, H_2SO_4 (after 20 hours).

sulfuric acid indicates that the carbonyl group is not removed in the manner indicated in Equation 1.



Division of the carbonyl double bond would lead to the formation of an hydroxyl group and the resulting compound might be expected to show (Equation 2) at least a tendency toward

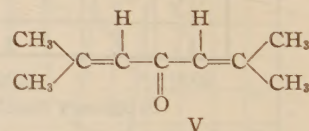
the same behavior as is observed with the aromatic triaryl carbinols (Equation 3).



Upon addition of a color producing agent, triaryl carbinols are known to give rise to entirely new absorption bands where none previously existed.⁷ This is not the case for simple aromatic ketones since no new bands appear and, on this basis also, one concludes that the carbonyl double bond is still present in the colored solutions. On the basis of the foregoing observations, the structure indicated in $\left[\text{R}-\overset{\text{R}}{\underset{\text{R}}{\text{C}}}=\text{OH} \right]^+ \text{OSO}_3\text{H}^-$ IV does not appear unreasonable for the halochromic aromatic ketones of the benzophenone type.⁸

Other investigators have found that sulfuric acid solutions of unsaturated ketones of the type of dibenzalacetone give rise to entirely different light absorption from that of the saturated aliphatic and aromatic types of ketones. Several authors⁹ have pointed out the similarity existing between the colored solutions of unsaturated ketones and aromatic carbinols. It is interesting to note in the literature that phorone (V)¹⁰ when dissolved in sulfuric acid shows only simple enhancement of the carbonyl band.

This seems to indicate that the presence of double bonds is not the only factor involved in the absorption changes noted



(7) Anderson, *THIS JOURNAL*, **52**, 4567 (1930); Schoepfle and Ryan, *ibid.*, **54**, 3687 (1932).

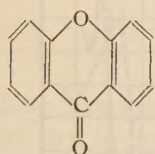
(8) A formula which differs from this one by having a single bond between the C and O has been suggested and discussed by other writers, including, for example, Dilthey (*J. prakt. Chem.*, [2] **109**, 303 (1925)) and Wizinger (*Z. angew. Chem.*, **40**, 939 (1927)). In the structure as we picture it, the double bond is present as in the simple ketones and if, in the simple ketones, there is "polar activation" of the carbonyl bond as ascribed by Lowry (*J. Chem. Soc.*, **123**, 822 (1923); 620 (1926)) and conversion of the non-polar into a semi-polar double bond: $\text{>C=O} \rightleftharpoons \text{>C}^+-\text{O}^-$, we suggest that true halochromism involves a shift of this equilibrium toward the right (see also, Watson, Nathan and Lourie, *J. Chem. Physics*, **3**, 170 (1935)). The hydrogen ion is probably linked to the carbonyl oxygen in the same manner as it is linked to the oxygen of water in the hydronium ion $[\text{H}_2\text{OH}]^+$ and to N in the ammonium ion $[\text{H}_4\text{NH}]^+$.

(9) Baker, *J. Chem. Soc.*, **91**, 1491 (1907); Lifschitz and Lourie, *Z. wiss. Phot.*, **16**, 269 (1917); Kehrmann and Efront, *Ber.*, **54**, 417 (1921); Hantzsch, *ibid.*, **55**, 954 (1922); Kauffmann, *ibid.*, **55**, 1967 (1922).

(10) Baly, Collie and Watson, *J. Chem. Soc.*, **95**, 144 (1909) Scheibe, *Ber.*, **58**, 594 (1925).

for dibenzalacetone and that the presence of phenyl groups is also required.

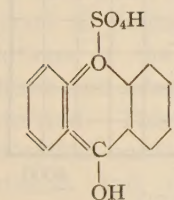
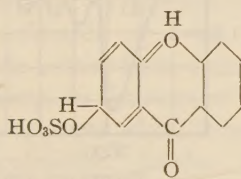
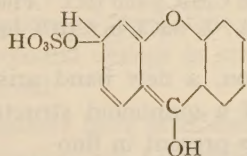
Xanthone contains a carbonyl group of which the carbon atom is a part of a six-membered ring containing oxygen. Anderson¹¹ has found that a solution of xanthone in sulfuric acid shows enhancement of the carbonyl group in harmony with the results obtained for the ketones previously discussed. However, it also possesses a new band appearing in the visible region and this new band was attributed to a stabilization of the quinone structure for xanthone (VI). We have



VI

now found that stannic chloride in ethylene chloride brings about an identical change (Fig. 6). Even dry hydrogen chloride is capable of this stabilization to a small extent. This reactivity with hydrogen chloride is not found in the other ketones studied and is presumed to be a result of the influence of the ortho bridge oxygen upon the 9-carbon of xanthone.

It was deemed advisable to investigate the absorption spectra of sulfuric acid solutions of aromatic ethers in connection with possible oxonium formation at the ether oxygen of xanthone, Formulas VII and VIII, a mechanism which several workers have preferred instead of quinoidation (Formulas IX and XI), especially in relation to the constitution of the salts of pyrone and its derivatives.

VII (Oxonium, *o*-quinonoid)VIII (Oxonium, *p*-quinonoid)

IX (Quinonoid, no carbonyl)

Pfeiffer's¹² work has shown that only one oxygen in xanthone takes part in addition reactions with color producing agents and that xanthone conforms exactly to the molecular ratios found

between a large number of other ketones not possessing an additional oxygen atom and the acids or metal halides, and he concludes that, in xanthone, the carbonyl oxygen is the reactive one.

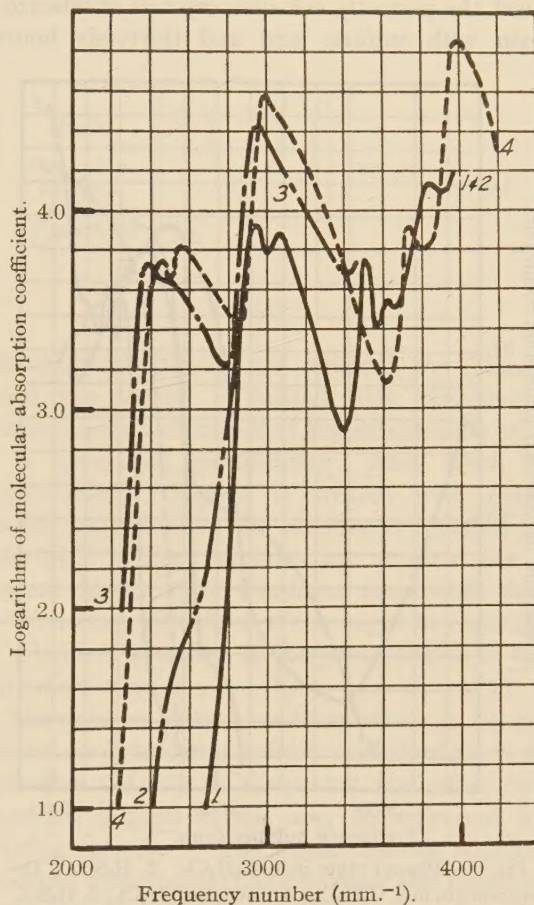
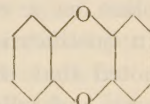


Fig. 6.—Xanthone: 1, $C_2H_4Cl_2$; 2, $C_2H_4Cl_2 + HCl$; 3, $SnCl_4$ in $C_2H_4Cl_2 + HCl$; 4, H_2SO_4 .

The absorption curves for diphenyl ether in ethylene dichloride and in sulfuric acid are given in Fig. 7. In sulfuric acid solution the group of narrow bands becomes one broad band and there is a slight displacement of the absorption toward the longer wave lengths; the latter change is not unusual, as is to be noted in our work with the ketones. No new bands appear in the sulfuric acid solution which could account for the bands formed near the visible region in the xanthone absorption spectra.

The report that dibenzodioxin, X, dissolves in concentrated sulfuric acid to produce an intensely blue colored solution is of interest, especially as regards xanthone. The position of an absorption band for this solu-



(11) Anderson, *THIS JOURNAL*, **55**, 2094 (1933).

(12) Pfeiffer, "Organische Molekulverbindungen," Stuttgart, Germany, 1922, p. 66.

tion was determined by Moir.¹³ He states that the temperatures were too low and the observations made too quickly for sulfonation to have taken place. In our experiments it was difficult to wet the perfectly colorless crystals of dibenzodioxin with sulfuric acid and thirty-six hours

with formation of oxidation products accompanied by pronounced color changes. It seems obvious, therefore, that the appearance of color upon dissolving dibenzodioxin in sulfuric acid is not related to the question of the color of corresponding solutions of xanthone.

The absorption curves for sulfuric acid solutions of fluorenone show changes similar to those noted for xanthone (Fig. 8). They, like xanthone, show normal enhancement of the carbonyl band

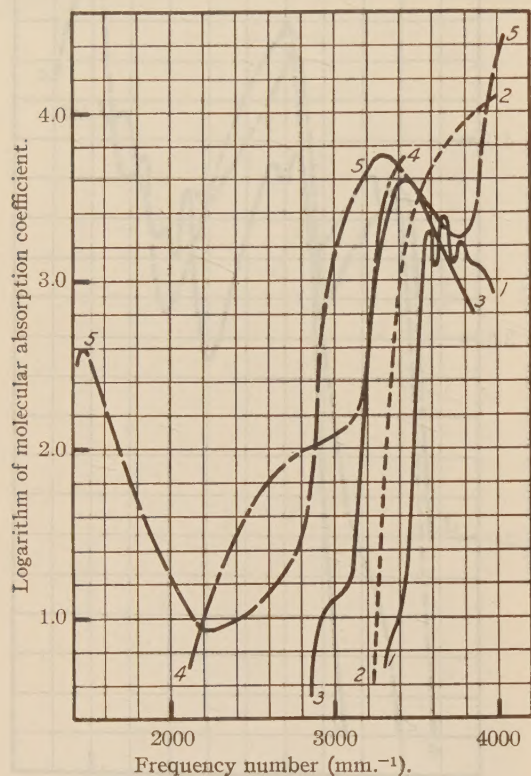


Fig. 7.—Phenyl ether in 1, $C_2H_4Cl_2$; 2, H_2SO_4 . Dibenzodioxin in 3, $C_2H_4Cl_2$; 4, $SnCl_4$ in $C_2H_4Cl_2$; 5, H_2SO_4 .

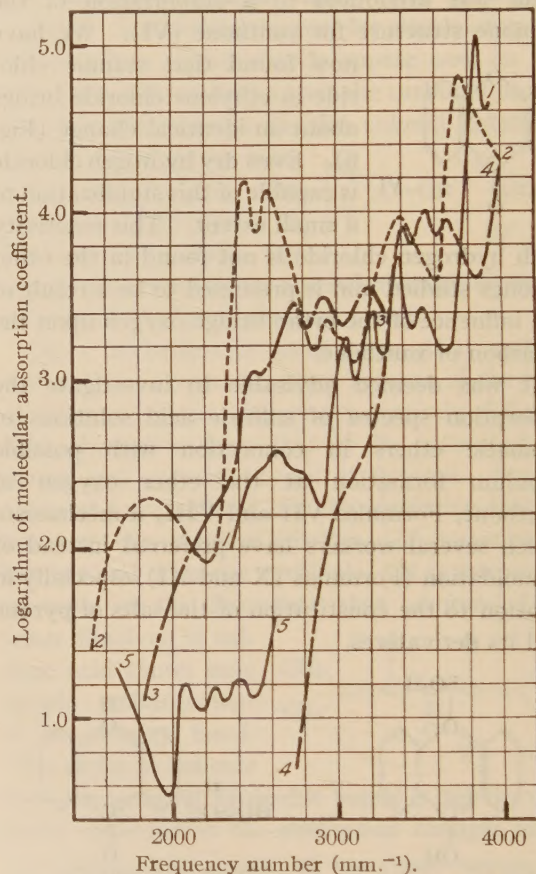
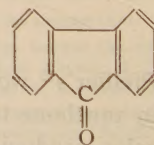


Fig. 8.—Fluorenone: 1, $C_2H_4Cl_2$ and HCl ; 2, H_2SO_4 ; 3, $SnCl_4$ in $C_2H_4Cl_2$ and HCl . Fluorenone chloride: 4, $CHCl_3$; 5, $SnCl_4$ in $CHCl_3$ (qualitative).

did not suffice to dissolve 20 mg. in 25 cc. of acid in a closed flask on a shaking machine. However, when 2 g. was vigorously stirred with 100 cc. of acid in air, complete solution was accomplished in seven hours. Using these solutions, we were able to check the one absorption maximum in the visible region of the spectrum recorded by Moir (Fig. 8). When the solutions were poured into twice their volumes of water at a temperature not exceeding 30° , no dibenzodioxin was recovered although it is very insoluble. It appears that solution must have taken place as a result of sulfonation or oxidation. In justification of this conclusion it may be noted that the corresponding monosulfur, selenium, and tellurium cyclic compounds have been shown by Drew¹⁴ to dissolve in sulfuric acid

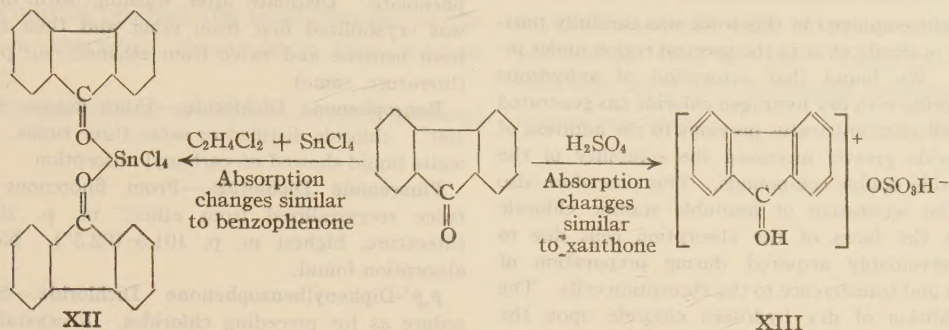
and, in addition, a new band arising from the stabilization of a quinonoid structure, XI. No ether oxygen is present in fluorenone and yet it exhibits the same type of color formation associated with solutions of xanthone in sulfuric acid. However, in the absence of the bridge oxygen, the carbonyl group resembles that of benzophenone more than that of xanthone in its reaction with stannic chloride in ethylene chloride



(13) Moir, *Trans. Roy. Soc. S. Africa*, **18**, Pt. 2, 137 (1929).

(14) Drew, *J. Chem. Soc.*, 3054 (1926); *ibid.*, 506 (1928).

solution. The absorption curve in this solvent indicates only slight formation of a quinonoid addition compound. These relations may be illustrated in the following manner



Like benzophenone, its absorption is unaltered by dry hydrogen chloride at room temperature.

Ketone chlorides are capable of undergoing changes in structure under the influence of an agent which produces color, because direct union of the agent with the central carbon atom is possible in absence of the stable double bond found in ketones. It was found that changing from an indifferent solvent like ethylene dichloride to a color-producing solvent like sulfuric acid or ethylene dichloride containing stannic chloride produces changes in the absorption curve of the ketone chloride which are different from those noted in the case of the parent ketone. Intensely colored solutions are obtained which have absorption bands far out in the visible region beyond all limits of absorption by the colorless solutions of the ketone chloride or even the sulfuric acid solutions of the ketone from which it is derived. This same change in the form of the absorption curve always appears when triarylcarbinols and the triarylmethyl halides are similarly treated. As in the case of the latter substances, the appearance of the new bands in the colored solutions of the ketone chlorides suggests that a profound change in structure of the solute has occurred.

Some investigators have attributed these color changes to ionization but Lifschitz and Girbes¹⁵ have pointed out that the cause for the altered light absorption cannot be ionization alone. It appears necessary, therefore, to assume formation of a new chromophore. A convenient and very probable configuration is that of a quinonoid structure for one of the phenyl groups,

(15) Lifschitz and Girbes, *Ber.*, **61**, 1484 (1928).

The ease with which the bromine atoms in 4,4'-

dibromobenzophenone are replaced by chlorine when the ketone is heated with phosphorus pentachloride indicates that ketone chlorides exist in a quinonoid modification. Also, when *p*-bromobenzoyl chloride is treated with phosphorus pentachloride the bromine is replaced by chlorine.¹⁶ These reactions are unusual for a normal ring-substituted halogen atom while they are in accord with those which might be expected of a halogen attached to the para position in the quinonoid ring.

The intense colors resulting when a ketone chloride is dissolved in sulfuric acid slowly fade as hydrogen chloride is eliminated and after two days the original ketone may be recovered by pouring upon ice.¹⁷ The ketone chloride addition products with stannic chloride were also found to decompose in solution at rates somewhat dependent upon the solvent employed. The curves for benzophenone chloride (Fig. 4) are quantitative. Those for fluorenone chloride and *p,p'*-diphenylbenzophenone dichloride are qualitative, since the solutions were not stable.

Several double compounds were prepared from ketones and mercuric chloride. The absorption curves for their solutions were found to show no noticeable difference from those of the free ketone or quinone, and the results appear to indicate that these double compounds are dissociated in solution. Measurements were made on solutions of the double compounds which were weighed out as such and also upon solutions prepared by addition of the organic component to a solution containing excess of the mercuric chloride. No

(16) Cone and Long, *THIS JOURNAL*, **28**, 518 (1906); Cone and Robinson, *Ber.*, **40**, 2160 (1907).

(17) Straus and Ecker, *Ber.*, **39**, 3005 (1906).

reduction of mercuric chloride to mercurous chloride was noticed since the solutions remained clear during the course of a determination.

Experimental

Each solvent employed in this work was carefully purified and was optically clear in the spectral region under investigation. We found that saturation of anhydrous ethylene chloride with dry hydrogen chloride gas generated in a special all-glass apparatus previous to the addition of stannic chloride greatly increased the solubility of the stannic chloride double compounds. This procedure also prevented the separation of insoluble stannic chloride hydrates on the faces of the absorption cells due to moisture unavoidably acquired during preparation of the solutions and transference to the absorption cells. The effect of addition of dry hydrogen chloride upon the absorption spectrum of the solute as compared to that in the neutral solvent was determined and no change was observed except in the case of xanthone. The average of five separate titrations indicated the solvent to be 0.2 *N* with respect to hydrochloric acid.

Preparation of Solutes

Acetone.—First converted to bisulfite compound and after conversion back to ketone it was refluxed with and distilled from potassium permanganate. Refluxed with and distilled from calcium oxide; n_D^{15} 1.3621 (literature, n_D^{15} 1.3620).

Cyclohexanone.—Converted to bisulfite compound (three times); dried with calcium chloride, fractionated; b. p. 151–151.8° (739 mm.) (literature, b. p. 155.4° (760)).

3-Hexanone.—From Grignard reaction of $\text{CH}_3\text{CH}_2\text{CH}_2\text{MgBr} + \text{CH}_3\text{CH}_2\text{CN}$; ketone fractionated three times, n_D^{22} 1.3997; b. p. 118–119° (747 mm.) (literature, n_D^{22} 1.39899; b. p. 123–123.5° (765)).

Dicyclohexyl Ketone.—Oxidation by dilute chromic acid at 45–50° of dicyclohexylcarbinol which was prepared from cyclohexylmagnesium chloride and ethyl formate; ketone, b. p. 164–165° (33 mm.); n_D^{14} 1.4851 (literature, n_D^{14} 1.484).

Cyclohexyl Phenyl Ketone.—(1) Oxidation of carbinol from Grignard reaction of cyclohexyl-MgCl + $\text{C}_6\text{H}_5\text{CHO}$. (2) Grignard reaction of cyclohexyl-MgCl + $\text{C}_6\text{H}_5\text{CN}$; m. p. (both samples) 57.5–58.5° (highest value in literature, m. p. 59–60°).

Benzophenone.—Two distillations at 25 mm. pressure, then two crystallizations from ether; m. p. 48°.

***p*-Phenylbenzophenone.**—Friedel-Crafts reaction of benzoyl chloride + biphenyl + AlCl_3 in carbon disulfide. Biphenyl removed by steam distillation and petroleum ether extraction. Ketone crystallized from methanol, twice crystallized from ethanol and once from ether; m. p. 102–103° (literature, 102–103°).

***p,p'*-Diphenylbenzophenone.**—Friedel-Crafts reaction of carbonyl chloride + biphenyl + AlCl_3 in carbon disulfide. Ketone crystallized twice from toluene, three times from xylene and finally acetic acid; m. p. 233.5–234.5° (literature, highest m. p. 233.4°).

Fluorenone.—Eastman Kodak material crystallized successively from ethanol and ether; m. p. 83.8–84.3° (literature, same).

Xanthone.—Same as fluorenone, m. p. 174°.

Diphenyl Ether.—Three successive fractional crystallizations; b. p. 248.5–249.5° (745.5 mm.), m. p. 28° (literature, b. p. 252° (760), m. p. 26, 27, 29°).

Dibenzodioxin.—Dry distillation of potassium *o*-chlorophenolate. Distillate after washing with dilute alkali was crystallized first from ether and then successively from benzene and twice from ethanol; m. p. 119–120° (literature, same).

Benzophenone Dichloride.—From ketone + PCl_5 at 150°: chloride distilled *in vacuo* three times. The clear, white liquid showed no carbonyl absorption.

Fluorenone Dichloride.—From fluorenone + PCl_5 : twice recrystallized from ether; m. p. 102.3–103.3° (literature, highest m. p. 101.5–102.5°). No carbonyl absorption found.

***p,p'*-Diphenylbenzophenone Dichloride.**—Same procedure as for preceding chlorides. Recrystallized three times from ether; m. p. 135.7–137° (literature, same).

Benzophenone HgCl_2 .—From benzophenone + HgCl_2 in (1) ether and (2) alcohol. Products crystallized from ether; m. p. 78–79° with decomposition (literature, highest m. p., 81°). *Anal.* Calcd: Hg, 44.24. Found: Hg, 43.98.

Benzophenone HgBr_2 .—From alcohol solution containing 1 mole ketone + 2 moles HgBr_2 . Recrystallized three times from ethanol; m. p. 76° (decomposition). *Anal.* Calcd.: Hg, 36.98. Found: Hg, 37.64.

Fluorenone HgCl_2 .—From alcohol solutions of ketone and HgCl_2 ; m. p. 158–159°. K. H. Meyer¹⁸ describes a compound, fluorenone (HgCl_2)₂, as orange-red needles but no melting point is given. Starting with the proportions of 1 mole of fluorenone to 2 moles of HgCl_2 in alcohol solution, HgCl_2 was first precipitated followed by the orange-red crystals corresponding to the molecular ratio 1:1. *Anal.* Calcd.: Hg, 44.42; Cl, 15.70. Found: Hg, 44.75; Cl, 15.28.

Xanthone HgCl_2 .—From either acetic acid or alcohol solutions of xanthone and HgCl_2 as colorless needles melting at 229–230° to a light brown liquid. *Anal.* Calcd.: Hg, 42.9. Found: Hg, 42.97, 43.09.

Quinone HgCl_2 .—From alcohol solutions of quinone and HgCl_2 ; recrystallized orange-red needles from alcohol; m. p. 153–154° (decomposition). *Anal.* Calcd.: Hg, 52.85; Cl, 18.68. Found: Hg, 52.62; Cl, 18.51.

The quantitative absorption spectra and positions of maximum absorption (Table I) were obtained by methods which have been described.¹⁹

Summary

1. Solutions of the ketones: acetone, 3-hexanone, cyclohexanone, dicyclohexyl ketone, cyclohexyl phenyl ketone, benzophenone, *p*-phenylbenzophenone and *p,p'*-diphenylbenzophenone in sulfuric acid show increased light absorption in the region associated with the carbonyl group. They retain their ketonic structure in these solutions.

(18) K. H. Meyer, *Ber.*, **43**, 162 (1910).

(19) Anderson and Gomberg, *THIS JOURNAL*, **50**, 203 (1928); Anderson, *ibid.*, **51**, 1889 (1929).

2. In addition to showing the above change, xanthone and fluorenone possess new bands in sulfuric acid solutions which are believed to be associated with the stabilization of the quinonoid structure for these compounds. Solutions of stannic chloride produce the same changes on the absorption spectrum of xanthone that sulfuric acid does.

3. The production of color with xanthone and

sulfuric acid or stannic chloride is not due to the ether oxygen.

4. The color of ketone chlorides and sulfuric acid or stannic chloride is of a different nature from that of ketones and resembles that of triarylcabinols and salts of these carbinols. It is postulated that in such solutions the ketone chlorides exist in a quinonoid modification.

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